# PATENT ABSTRACTS OF JAPAN

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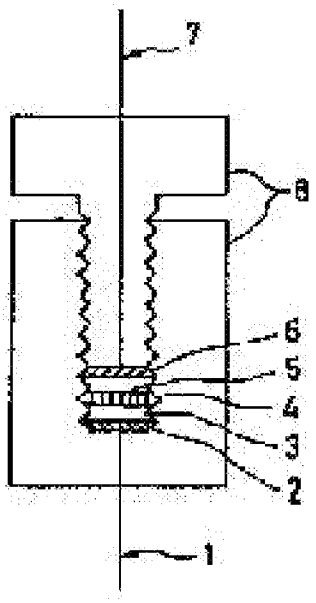
(54) **MANGANESE CELL**

(57)Abstract:

PURPOSE: To provide an aqueous solution type manganese cell of a discharge capacity larger than that of a conventional one, by using specified manganese dioxide for the positive electrode.

CONSTITUTION: Electrolytic manganese dioxide of more than 0.16 in mole number of water removed by a heat treatment in a temperature range from 120°C to 400°C per 1mol of Mn atoms is precipitated by electrolysis. The manganese dioxide is exfoliated from a titanium anode electrode, and crashed to powders. The manganese dioxide powders are mixed with conductive carbon powders and compression molded to a pellet. The pellet is used for the positive electrode 3 and a Zn piece is used for the negative electrode 5 of a manganese cell, and an electrolyte consisting of an aqueous solution of 40wt.% of KOH is impregnated in a separator 4 to construct the cell. As the result, the discharge capacity can be increased up to 31mAH from 20mAH of a



conventional one.

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## CLAIMS

[Claim(s)]
[Claim 1]A cell by which the number of mols of water removed by heat-treatment in a range which does not exceed not less than 120 ** 400 ** is characterized by using for an anode electrolytic manganese dioxide which is 0.16 or more [ per 1 mol of Mn atoms ].

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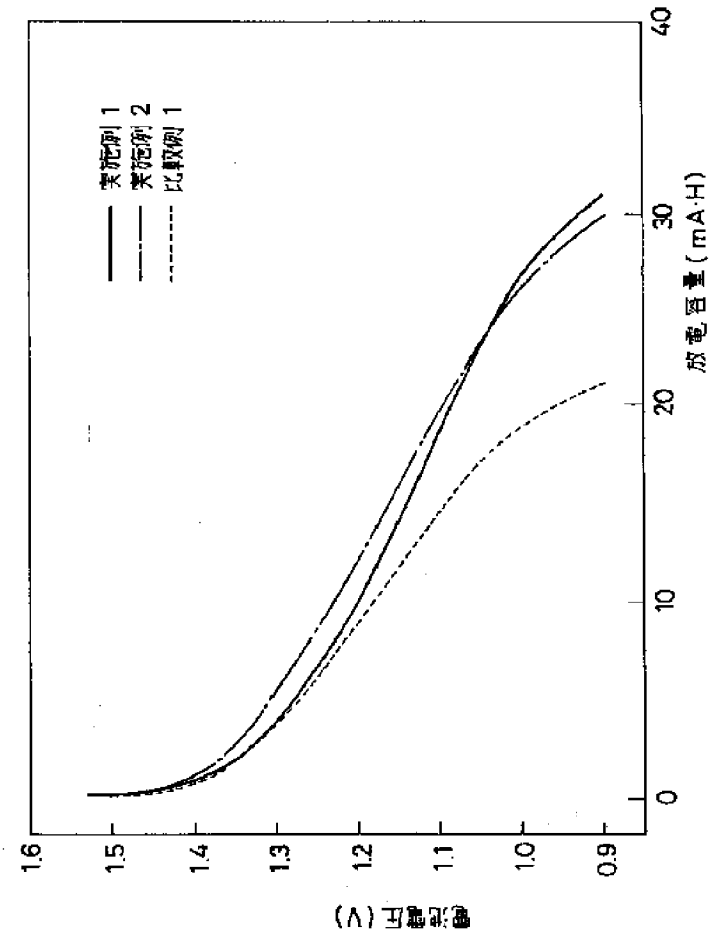


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## DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to the cell which uses manganese dioxide for an anode, and relates especially to highly efficient-ization of an aqueous solution system manganese cell.
[0002]
[Description of the Prior Art]The aqueous solution system cell which uses manganese dioxide for an anode is put in practical use for many years.
It can divide into a Leclanche cell, a zinc chloride series cell, and an alkaline manganese dioxide cell according to the kind of electrolysis solution to be used.

[0003]Also in these fuel cell subsystems, especially an alkaline manganese dioxide cell is an aqueous solution system manganese cell in which the performance was most excellent now, and the amount used is increasing steadily in recent years.
[0004]As one technical problem of highly-efficient-izing of

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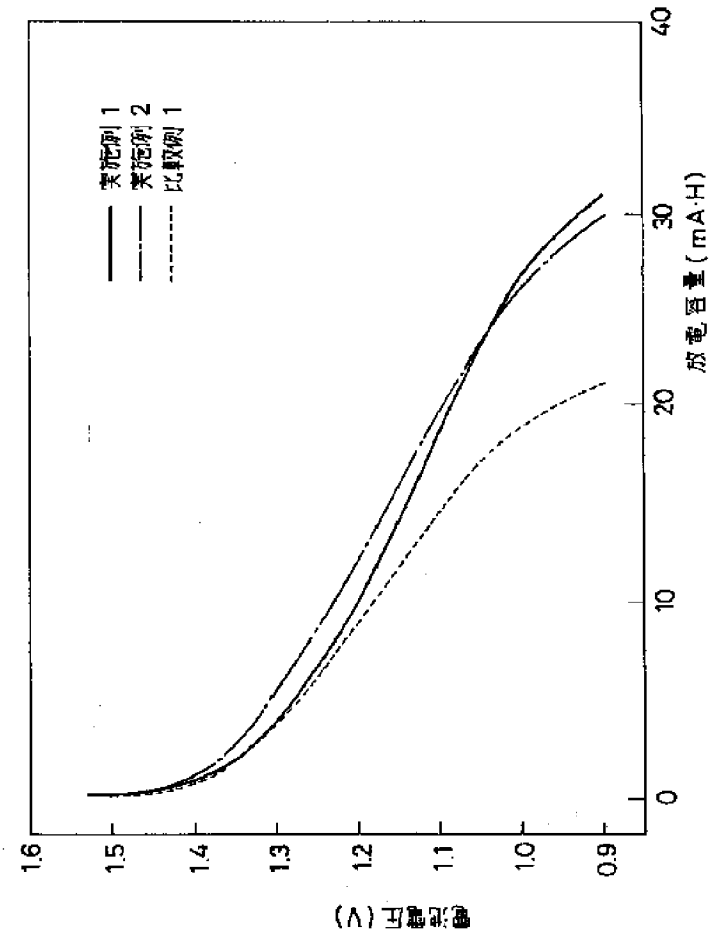


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an aqueous solution system manganese cell, improvement of manganese dioxide used for an anode has been advanced.
[0005]Although natural manganese dioxide was used for manganese dioxide at the beginning, synthetic manganese dioxide is used by development of synthetic manganese dioxide more highly efficient than a natural article for most aqueous solution system manganese cells now.
[0006]In particular, in the case of the most highly efficient alkaline manganese dioxide cell, electrolytic manganese dioxide which is one kind of synthetic manganese dioxide is used for the anode of almost all the cells.
[0007]On the other hand, from problems, such as earth environment, it is an environmental pollutant and regulation of use of the mercury used from the former for the improved efficiency of an aqueous solution system manganese cell and abolition-ization came to be considered recently.
[0008]For this reason, the problem said that the performance of an aqueous solution system manganese cell recently falls arises, and the further improved efficiency of manganese dioxide is considered.
[0009]
[Problem(s) to be Solved by the Invention]The purpose of this invention is to use specific manganese dioxide for an anode and to provide an aqueous solution system manganese cell with big service capacity.
[0010]
[Means for Solving the Problem]The number of mols of water removed by heat-treatment in a range which does not exceed not less than 120 ** 400 ** as a result of repeating examination wholeheartedly in view of such a situation this invention persons, It finds out that an aforementioned problem can solve 0.16 or more [ per 1 mol of Mn atoms ] electrolytic manganese dioxide by using for an anode, and came to complete this invention.
[0011]Service capacity becomes large when the number of mols of water removed by heat-treatment in a range which does not exceed not less than 120 ** 400 ** uses 0.16 or more [ per 1 mol of Mn atoms ] electrolytic manganese dioxide for an anode compared with less than 0.16 electrolytic manganese dioxide.
[0012]Therefore, if manganese dioxide of this invention is used for an anode, an aqueous solution system manganese cell with larger service capacity than before can be constituted.
[0013]
[Function]Hereafter, this invention is explained concretely.
[0014]Especially the water removed by heat-treatment in the range which does not exceed not less than 120 ** 400 ** of this invention is important for the discharging performance

of an aqueous solution system manganese cell.
[0015]The discharge reaction of an aqueous solution system manganese cell advances by the generation reaction of MnOOH and the reduction reaction of Mn atom by the proton ($H^+$) diffusion from a battery electrolytic solution inside the manganese dioxide solid phase.
[0016]It is strongly influenced with existence of water and abundance, and it is so easy to be spread that diffusion of a proton has much abundance.
[0017]In particular, since a proton diffusion reaction and the reduction reaction of Mn atom advance simultaneously, discharging performance is excellent in a discharge reaction, so that Mn atom and water with an interaction are important for a discharge reaction and there is much abundance of this water.
[0018]That is, since a discharge reaction becomes easy and also a reaction advances to all the corners of an anode so that there is much quantity of Mn atom and water with an interaction, the utilization efficiency of an anode becomes high, and discharging performance improves.
[0019]Although the water removed by heat-treatment in the range which does not exceed not less than 120 ** 400 ** is unknown about details, it is water which has Mn atom and a certain interaction, and also can be contributed to a discharge reaction.
[0020]The water removed by heat-treatment below 120 ** is the water which carried out physical adsorption, and does not only have Mn atom and an interaction in the manganese dioxide particle surface.
[0021]Since the water removed by heat-treatment over 400 ** has Mn atom and a firm interaction, it cannot participate in a discharge reaction.
[0022]That is, the water removed by heat-treatment in the range which does not exceed not less than 120 ** 400 ** is water which has Mn atom and an interaction and can be contributed to a discharge reaction.
It is important for the discharging performance of an aqueous solution system manganese cell.

[0023]The number of mols of the water removed by heat-treatment in the range which does not exceed not less than 120 ** 400 ** of this invention is important for the discharging performance of an aqueous solution system manganese cell.
[0024]Although it is unknown about details, it becomes difficult to produce the diffusion reaction within solid phase by proton hopping to which the number of mols of water passed water or less [ per 1 mol of Mn atoms ] by 0.16, and it becomes impossible for the proton ($H^+$) diffusion inside

the manganese dioxide solid phase to advance easily according to this invention persons' examination. For this reason, in order to perform a discharge reaction smoothly, the quantity of water of 0.16 mol [ per mol of Mn atom ] or more is required.

[0025]Heat-treatment of this invention is performed in the atmosphere. By heat-treating in the atmosphere, the quantity of the water which has Mn atom and an interaction and can be contributed to a discharge reaction can be evaluated correctly.

[0026]Electrolytic manganese dioxide of this invention is manufactured with the usual electrolytic method using the acidic solution which contains divalent manganese salt in an electrolysis solution.

[0027]For example, using titanium, carbon, etc. for the anode, using carbon etc. for the negative pole as an electrode, and electrolyzing, using the solution of manganese sulfate and sulfuric acid as an electrolysis solution, is illustrated.

[0028]By combining arbitrarily the monograph affair of the divalent manganese salt concentration of the above-mentioned electrolysis solution, acid concentration, electrolysis temperature, and electrolytic current density, The number of mols of the water removed by heat-treatment in the range which does not exceed not less than 120 ** 400 ** of a request can obtain 0.16 or more [ per 1 mol of Mn atoms ] electrolytic manganese dioxide.

[0029]Electrolytic manganese dioxide of this invention was used for the anode, and the model cell shown in drawing 1 was constituted.

[0030]The number of mols of the water removed by heat-treatment in the range which does not exceed not less than 120 ** 400 **, When 0.16 or more [ per 1 mol of Mn atoms ] electrolytic manganese dioxide was used for the anode, the model cell was made as an experiment and service capacity was investigated, compared with the service capacity of the model cell made as an experiment using less than 0.16 electrolytic manganese dioxide, it turned out that big service capacity is shown.

[0031]

[Example]Hereafter, although this invention is more concretely explained based on an example and a comparative example, this invention is not limited to this.

[0032]The number of mols of the water removed as example 1 (creation of electrolytic manganese dioxide) Example 1 by heat-treatment in the range which does not exceed not less than 120 ** 400 ** created 0.16 or more [ per 1 mol of Mn atoms ] electrolytic manganese dioxide as follows.

[0033]Manganese dioxide was deposited on titanium which

is the anode by using titanium for the anode, using carbon for the negative pole, and electrolyzing with the current density of 0.5 A/dm$^2$ in the solution which contains manganese sulfate in 0.6 mol [ l. ] /, and contains sulfuric acid by the concentration of 0.3 mol/l. From the titanium electrode, it exfoliated, deposit manganese dioxide was ground, and it powdered. 70 g of this powder sample was put into the atmosphere release type electric furnace, heat-treatment was performed at 120 ** for 16 hours, and physical-adsorption water was removed. It cooled radiationally to the room temperature after heat-treatment and within the dry desiccator, and sample weight was measured in a drying atmosphere. The sample weight at this time was 69.3g. Next, the sample which carried out 16 time processings at these 120 ** is put into an atmosphere release type electric furnace, heat-treatment is performed at 400 ** for 2 hours, it has Mn atom and an interaction, and the water contributed to a discharge reaction was removed. The sample was cooled radiationally to the room temperature within the dry desiccator after processing, and sample weight was measured in a drying atmosphere. The sample weight at this time was 67g.

[0034]It was 0.17 when the number of mols of the water per 1 mol of Mn atoms was calculated from the amount of weight changes between the two above-mentioned heating samples.

(The composition of a cell), next these manganese dioxide powders and the carbon powder of a conducting agent were mixed at a rate of 2:1 by the weight ratio. 300 mg of this mixture was molded into the pellet of 13 mmphi by the pressure of 5 ton/cm$^2$. In the electrolysis solution, the model cell which impregnates with 40wt%KOH solution at the separator of 4 of drawing 1, and shows it to drawing 1 was constituted, using the piece of Zn in the negative electrode of 5 of drawing 1, using this as an anode of 3 of drawing 1. (Battery capacity evaluation) Using the cell created with the described method, continuous discharge was performed until cell voltage showed 0.9V with the constant current value of 26 mA. The result of the spark test was shown in drawing 2. As a result, service capacity was 31mAh.

[0035]Example 2.

(Creation of electrolytic manganese dioxide) As Example 2, in the solution which contains manganese sulfate in 0.6 mol [ l. ] /, and contains sulfuric acid by the concentration of 0.3 mol/l., Manganese dioxide was deposited on titanium which is the anode by using titanium for the anode, using carbon for the negative pole, and electrolyzing with the current density of 0.8 A/dm$^2$. After having exfoliated, grinding deposit manganese dioxide from the titanium electrode and

powdering, as a result of performing the same heat-treatment as Example 1, the number of mols of the water per 1 mol of Mn atoms was 0.18.

[0036]Next, the same cell as Example 1 was constituted except having used this for the anode of 3 of drawing 1. The result of battery characteristic evaluation was shown in drawing 2. Service capacity was 30mAh.

[0037]As the comparative example 1 comparative example 1, in the solution which contains manganese sulfate in 0.6 mol [ l. ] /, and contains sulfuric acid by the concentration of 0.3 mol/l., The number of mols of the water per 1 mol of Mn atoms obtained manganese dioxide of 0.14 by using titanium for the anode, using carbon for the negative pole, and electrolyzing with the current density of 0.2 A/$dm^2$. Except having used this manganese dioxide for the anode of 3 of drawing 1, the same cell as Example 1 was constituted, and the result of having evaluated the battery characteristic was shown in drawing 2. Service capacity was 21mAh.

[0038]

[Effect of the Invention]The manganese cell of this invention has big service capacity.

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